The Dimerization Reaction of Propylene by Nickel Acetylacetonate-Triethylaluminum Sesequichloride-Tertiary Phosphine Catalyst : Electronic and Steric Effect of Phosphorous Ligands (Commemoration Issue Dedicated to Professor Sango Kunichika On the Occasion of his Retirement)

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The Dimerization Reaction of Propylene by Nickel Acetylacetonate—Triethylaluminum Sesequichloride—Tertiary Phosphine Catalyst. Electronic and Steric Effect of Phosphorous Ligands.*

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In the dimerization reaction of propylene in toluene by nickel acetylacetonate—triethylaluminum sesequichloride—tertiary phosphine catalyst, the effect of the nature of phosphorous ligands has been studied. In the range of five triarylphosphines, $P(-C_6H_4-X)_3$: X=*p*-Cl, *p*-H, *p*-CH_3, *p*-OCH_3, and *o*-CH_3, their electronic effect on the dimer distribution was rather small, while in the case of *o*-CH_3, a large steric effect was observed, giving a high yield of 2,3-dimethylbutenes. The activity of this kind of catalyst decreased in the following order: *p*-Cl>*p*-H>*o*-$CH_3 \simeq$ *p*-CH_3>*p*-OCH_3>PEt_3>$P(n\text{-}Bu)_3$. Based on the experimental results, a reaction mechanism involving the participation of a square planar nickel hydride complex is proposed, which reasonably explains the effect of phosphines on the dimer distribution.

INTRODUCTION

In our previous paper,[1] the effect of reaction conditions on the dimerization reaction of propylene by $Ni(acac)_2$-$Al_2(C_2H_5)_3Cl_3$-$P(C_6H_5)_3$ catalyst was investigated, and based on the results, a reaction mechanism, in which nickel hydride complexes are considered to be the active catalytic species, was proposed. This paper mainly deals with the electronic and steric effects of phosphorous ligands on the dimer distribution in relation to the reaction mechanism.

Concerning the effect of phosphines on the dimerization reaction by nickel complexes, Wilke, *et al.*[2] and Lefebvre, *et al.*[3] have reported that the basicity of phosphines favors the formation of 2,3-dimethylbutenes but not that of hexenes. Besides, they have suggested that the bulkiness of phosphines appears to affect the dimer distribution considerably. In this investigation, an attempt was made to examine the influence of electronic and steric factors of phosphines on the dimerization reaction, especially the dimer distribution, by using several tri-*p* and *o*-substituted phenylphosphines and trialkylphosphines. Such a study would help not only to infer the nature of true active species in the reaction, but also to predict the product distribution.

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EXPERIMENTAL

Reagents. Toluene was purified and dried by the ordinary method. Propylene (99.0 mol % pure), nickel acetylacetonate, and triethylaluminum sesequichloride were obtained from commercial sources. Triethylphosphine:[4] b.p. 127°, tri-*p*-anisyl-phosphine:[5,6] m.p. 131°, tri-*p*-tolylphosphine:[5] m.p. 146°, tri-*o*-tolylphosphine:[5] m.p. 124°, and tri-*p*-chlorophenyl-phosphine:[5] m.p. 102°, were prepared from the corresponding Grignard's reagents and phosphorous trichloride, and proved to be sufficiently pure by the elemental analysis. The other phosphines, tri-*n*-butylphosphine and triphenylphosphine, were commercially available and used without further purification.

Procedures of Dimerization. Two reaction procedures (A) and (B) were employed. Each representative one is exemplified.

Procedure (A): In a 200-ml four-necked, round-bottomed flask fitted with a thermometer, a propylene inlet glass tube, and three-way cock, were placed 52 mg (0.2 mmol) of nickel acetylacetonate, 840 mg (3.2 mmol) of triphenylphosphine, and 100 ml of toluene under nitrogen atmosphere. The mixture was stirred magnetically at 20° (identical to dimerization temperature) and 2.5 g (9 mmol) of triethylaluminum sesequichloride was added dropwise through the cock using a glass syringe. Thus, a red-brown catalyst solution was obtained. Propylene (10 g), reserved in a glass pressure vessel, was introduced to the catalyst solution from the inlet tube over 1.0 hr at 20° and atmospheric pressure, and then, further stirring was continued for 0.5 hr at the temperature. The reaction mixture was quenched with a mixture of methanol (20 ml) and conc. hydrochloric acid (30 ml). During all the period, unreacted propylene was collected in a water gas holder. The toluene layer was separated, washed with water, dried over $CaCl_2$, and analyzed by gas chromatography.

Procedure (B): A propylene solution was prepared by dissolving propylene (ca. 10 g) in toluene (120 ml) placed in a 200 ml four-necked flask, fitted with a glass connection tube in addition to the same fittings as designated in the procedure (A), at —40° or lower under nitrogen atmosphere. In another 50-ml flask, a catalyst solution, consisting of toluene (30 ml), nickel acetylacetonate (0.2 mmol), tertiary phosphine (3 2 mmol), and triethylaluminum sesequichloride (9 mmol), was prepared at the temperature used for the dimerization in the same manner as described above. By adding the catalyst solution to the propylene solution at a time through the connection tube, the reaction was started at —40° and continued for 1.0 hr. The mixture was quenched as described in the procedure (A). To estimate the initial product of the reaction by the zero conversion method, small portions (ca. 2 ml) of the reaction mixture was syringed out and quenched quickly at intervals. The quenched sample was treated as described in the procedure (A) and analyzed.

Analytical Method. The dimerization products were analyzed by gas chromatography (Shimadzu, GC-4AIT) using a 10-m sebaconitrile column at room temperature and with herium as a carrier gas. n-Heptane was used as an internal standard substance.

RESULTS AND DISCUSSION

Effect of Phosphine Component on the Dimer Distribution. A series

of experiments was made by varying the phosphine component in the catalyst of Ni (acac)$_2$: $Al_2Et_3Cl_3$: PR_3 (afterwards abbreviated as Ni : Al_2 : P) = 1 : 45 : 16 (Ni = 0.2 mmol) at 20 and −40°. Five triarylphosphines, P(- )$_3$: X=*p*-Cl, *p*-H, *p*-CH_3, *p*-OCH_3, and *o*-CH_3, and two trialkylphosphines, PEt_3 and P(*n*-Bu)$_3$, were used. The effect of the phosphines on the conversion, dimer selectivity, and dimer distribution at 20 and −40° is shown in Fig. 1 and Fig. 2, respectively.

The dimer distribution was presented by classifying all the resulting dimers (twelve kinds of C_6-olefins)[1] into three groups according to their carbon skeleton: 2-methylpentenes (2-MPs), 2,3-dimethylbutenes (2,3-DMBs), and *n*-hexenes (Hs). As a measure of the basicity of phosphines, the infrared CO stretching frequencies (ν_{CO}) of $Ni(CO)_3PR_3$[7] were adopted. Figure 1 and 2 suggest that the basicity of phosphines favors the formation of 2,3-DMBs and not that of Hs. For example, at −40° 2,3-DMBs increased with the increasing basicity from 2% for *p*-Cl to 23% for P(*n*-Bu)$_3$, while Hs and 2-MPs decreased from 20 to 9% and from 78 to 65%, respectively.

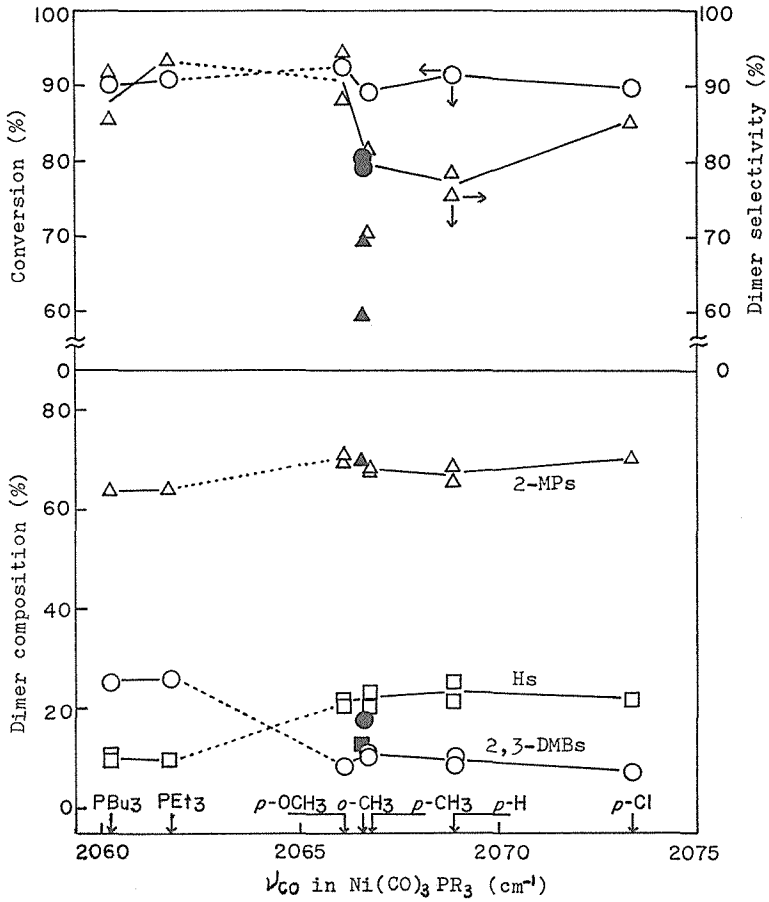


Fig. 1. Effect of phosphines at 20°.

Reaction was made by Procedure A. Ni(acac)$_2$ 0.2 mmol, Ni : Al_2 : P=1 : 45 : 16, Toluene 100 ml, Propylene 10.0 g, Time 1.5 hrs (0.5 hr continued after introducing propylene over 1.0 hr). Filled marks (●, ▲, ■) are used for tri-*o*-tolylphosphine.

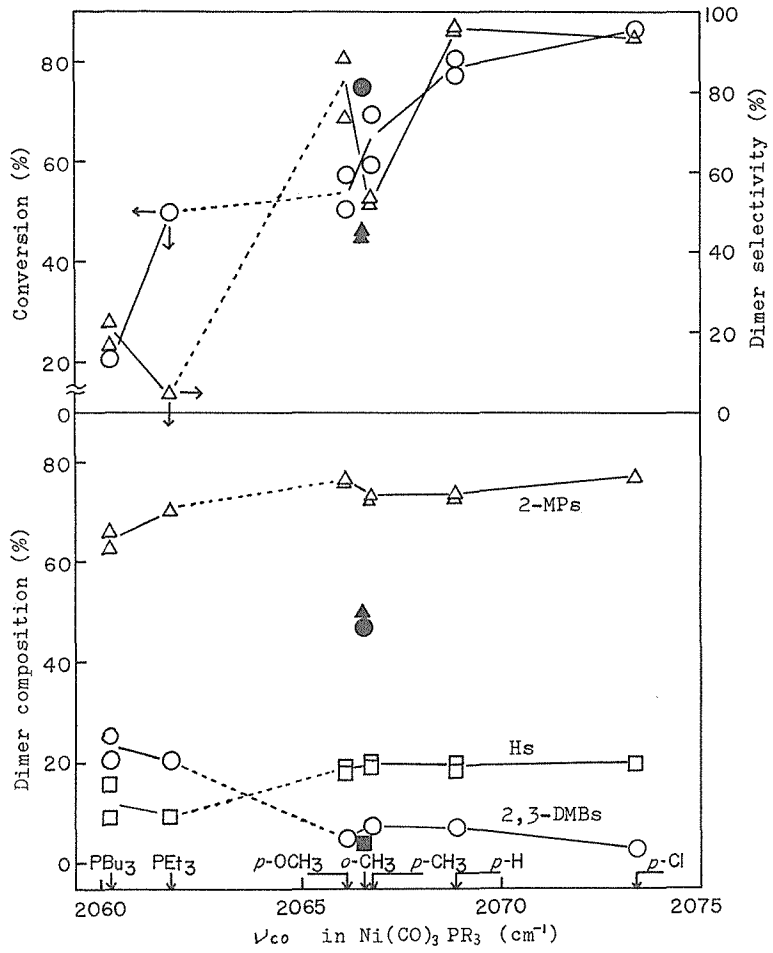


Fig. 2. Effect of phosphines at −40°.

Reaction was made by Procedure B. $Ni(acac)_2$ 0.2 mmol, Ni : Al_2 : P=1 : 45 : 16, Toluene 130 ml, Propylene 9.0 g, Time 1 hr. Filled marks (●, ▲, ■) are used for tri-*o*-tolylphosphine.

The product distribution for four tri-*p*-substituted phenylphosphines seems to reflect the electronic effect of phosphines, because their phosphines may be considered to be nearly equal in bulkiness. In practice, only a slight variation in the distribution was observed; 2,3-DMBs increased from 2% for *p*-Cl to 7% for *p*-CH_3 with the increasing basicity (Fig. 2). This result suggests that a strong electron-releasing *p*-substituent results in an increase of 2,3-DMBs though the effect is rather small within this phosphine range. On the contrary, a remarkable difference in the distribution between the *p*-CH_3 and *o*-CH_3 catalysts was observed; at −40°, 2,3-DMBs, Hs, and 2-MPs were 7, 19, and 74% for *p*-CH_3, and 46, 4, and 50% for *o*-CH_3, respectively (Fig. 2). This result implies the importance of the steric effect of phosphines, because both the phosphines have almost equal basicity. Concerning the bulkiness of phosphines, Tolman[8] measured the cone angles of various tertiary phosphines. According to his measurement, the cone angle

of tri-*o*-tolylphosphine, 194±6°, is fairly larger than that of tri-*p*-tolylphosphine, 145±2°. Thus, it may be concluded that a bulky phosphine results in an increase of 2,3-DMBs and a decrease of Hs. Here, a comparison of the dimer distribution between triethylphosphine and tri-*n*-butylphosphine would be very interesting. Since small cone angles of 132° for triethylphosphine and 130° for tri-*n*-butylphosphine, have been known, the effect may be attributed to the electronic nature of the phosphines. In conclusion, both the basicity and the bulkiness of phosphines favor the formation of 2,3-DMBs, but not that of Hs and 2-MPs. Thus, a high portion (67.9% in the dimer composition) of 2,3-DMBs for tri-*i*-propylphosphine, reported by Wilke, *et al.*[2a], seems to be due to its large bulkiness (160±10°) and strong basicity.

In the case of a series of tri-*p*-substituted phenylphosphines, 2,3-DMBs decreased with a decrease in the temperature, while 2-MPs increased, as in the case of triphenylphosphine reported previously.[1] However, the variations by the temperature were small. For example, with the *p*-Cl catalyst, 2,3-DMBs and 2-MPs were 7 and 71% at 20°, and 2 and 78% at −40°, respectively (Fig. 1 and 2). On the other hand, with *o*-CH_3, the reverse tendency was observed. Furthermore, a remarkable difference in the distribution between −20 and −40° was found, as shown in Fig. 3. 2,3-DMBs and 2-MPs varied from 18 and 74% at −20° respectively to 42 and 54% at −40°. Thus, the fact that the steric effect of tri-*o*-tolylphosphine is conspicuous especially at low temperature may be of great interest in connection with the structural behavior of the active catalytic species.

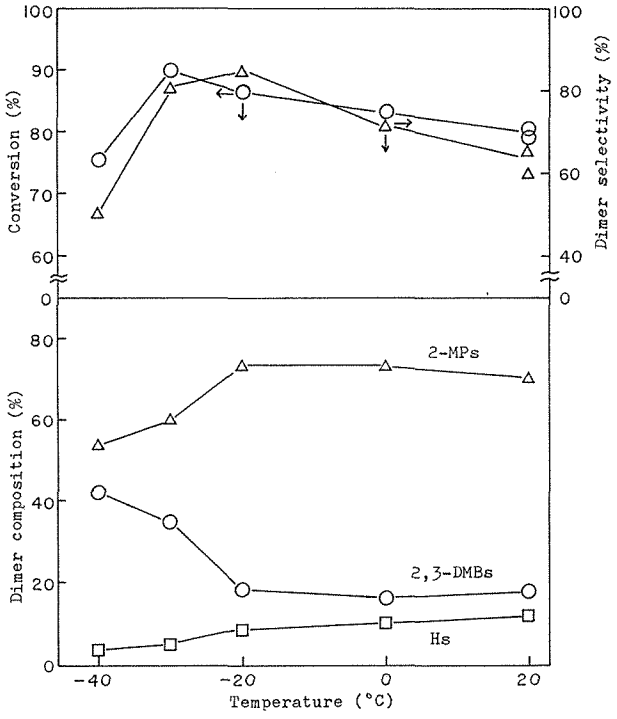


Fig. 3. Effect of temperature using tri-*o*-tolylphosphine.

Reaction was made by Procedure A. $Ni(acac)_2$ 0.2 mol, Ni : Al_2 : P=1 : 45 : 16, Toluene 100 ml, Propylene 10.0 g, Time 1.5 hrs.

Effect of Phosphine Component on the Reaction Rate. Distinct differences in the conversion of propylene between the phosphines used were observed at −40°, as shown in Fig. 2. Based on these conversion data, a decreasing order of the activity of this kind of catalyst agrees with the order of an increase in the electron-releasing ability of the phosphines and is as follows: *p*-Cl>*p*-H>*o*-CH_3≃*p*-CH_3>*p*-OCH_3> PEt_3>$P(n\text{-}Bu)_3$. In the rate of the isomerization of olefins by this kind of catalyst, the same order was observed, as already reported.[9] A decrease in the rate for a phosphine having a strong electron-releasing group is considered to be due to two reasons; 1) Ni-R (R = *i*-propyl or *n*-propyl) σ-bond in the active species ((II)∼(V) in Scheme 1 described below) which is assumed to participate in the rate-determining step,[1] is strengthened through an increase in the electron density on the formally Ni^{II} atom***, and 2) the concentration of the active species diminishes owing to an increase of an inactive species, which is assumed to be nickel complexes with two phosphines.[1] Unexpectedly, the conversions with the *p*-CH_3 and *o*-CH_3 catalysts were near by equal values, 69 and 74% respectively. Concerning the effect of phosphines on the reaction rate, a further study would be made.

Reaction Mechanism. A reaction mechanism for the dimerization is discussed

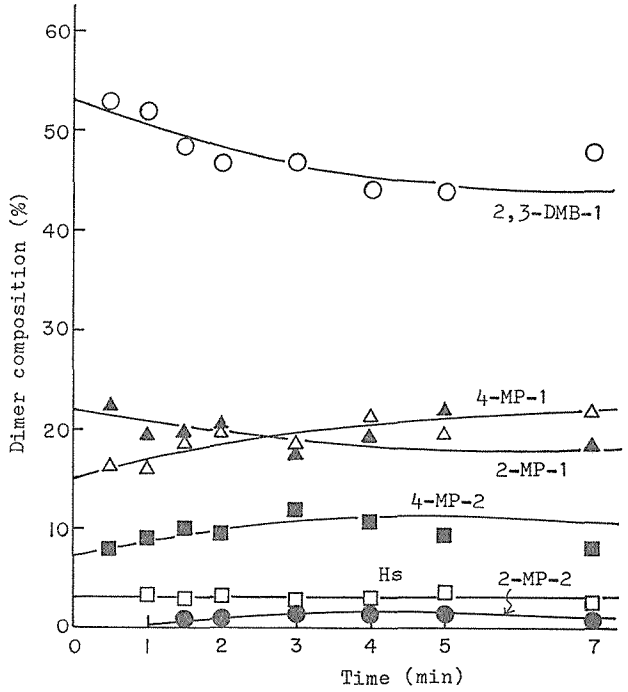


Fig. 4. Dimer distribution against reaction time using tri-*o*-tolylphosphine.

Reaction was made by Procedure B. $Ni(acac)_2$ 0.2 mmol, Ni : Al_2 : P=1 : 45 : 16, Toluene 150 ml, Propylene 10.9 g, −40°. The dimer yield at 5 min. was about 8%.

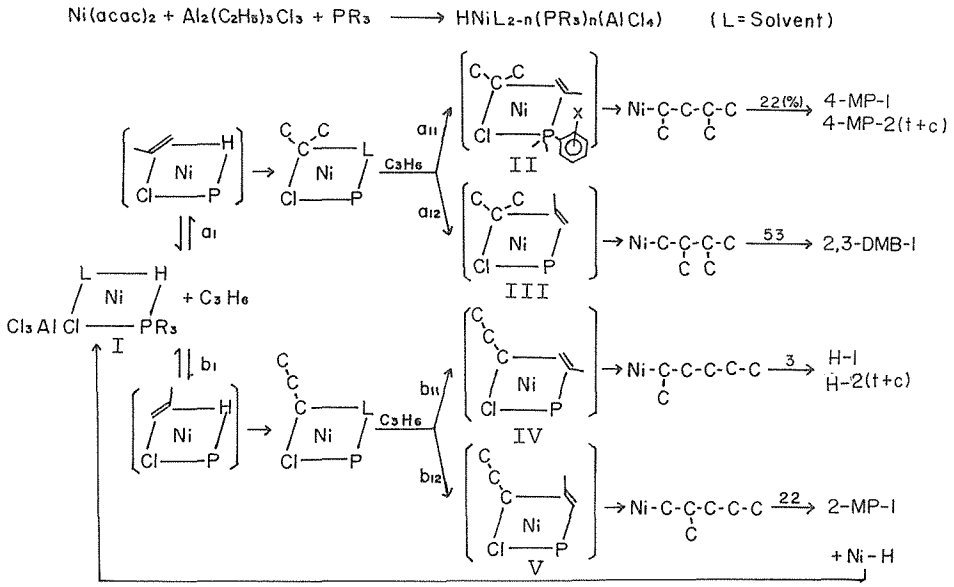
*** It is reported by Wilkinson, *et al.* that a strong electron-releasing phosphine strengthenes the Rh-H bonds in $Rh^{III}ClH_2(PR_3)_2$ (S. Montelatici, A. van der Ent, J.A. Osborn and G. Wilkinson, *J. Chem. Soc.* (*A*), **1968**, 1054).

in connection with the dimer distribution. First of all, the composition of primary products with tri-*o*-and tri-*p*-tolylphosphines was estimated by the zero conversion method. As an example, the case of tri-*o*-tolylphosphine is shown in Fig. 4. The estimated composition is listed in Table 1, toghther with that with triphenylphosphine. To account for the extraordinary result with tri-*o*-tolylphosphine, the following reaction mechanism was proposed. This mechanism is almost the same with that in our previous paper,[1] except that a specific square planar nickel hydride complex ((I) in Scheme 1) is suggested as the active catalytic species. Concerning their structure, two square planar isomer species (I) and (I′) with L(solvent) and hydrogen ligand in cis position may be hypothesized.[10]

Table 1. Composition of Primary Products[a]

Reaction Path in Scheme 1	Primary Products	Composition (%)		
		o-CH_3	*p*-CH_3[b]	*p*-H
a_1–a_{11}	4-MP-1	15 } 22	24 } 62	14 } 57
	4-MP-2	7	38	43
a_1–a_{12}	2,3-DMB-1	53	7	6
b_1–b_{11}	Hs	3	16	19
b_1–b_{12}	2-MP-1	22	15	18

a) The reaction conditions are described in Fig. 4.
b) This result, obtained at −50°C, was quoted from the previous paper[1].



Scheme 1. Mechanism of Dimerization

In this mechanism, however, the type (I) is favored over (I'), because the former is suitable for accounting for the steric effect of tri-*o*-tolylphosphine, as discussed below.

As shown in Table 1, a large $\%_{a_{11}}/\%_{a_{12}}$ ratio ($\%_{a_{11}}$ means the percentage of the dimer obtained via the path (a_{11})) of about 9 was given for the *p*-CH_3 and *p*-H catalysts, while the $\%_{b_{11}}/\%_{b_{12}}$ ratio was almost 1.0. This large ratio is supposed to be due largely to a slow reaction rate of the path (a_{12}), caused by the steric hindrance between the *i*-propyl group and the methyl group of co-ordinated propylene in the nickel complex (III). On the contrary, with *o*-CH_3, the $\%_{a_{11}}/\%_{a_{12}}$ ratio is small, being about 0.4, in spite of no significant differences in $\%_{a_1}$ between these three phosphines. This may be explained by assuming that the steric hindrance between the methyl group of co-ordinated propylene and the methyl group of tri-*o*-tolylphosphine in the nickel complex (II) is greater than the steric hindrance in the nickel complex (III) described above. Similarly, the difference in the $\%_{b_{11}}/\%_{b_{12}}$ ratio between *p*-CH_3 and *o*-CH_3 can be explained by a great steric hindrance existing in the nickel complex (IV) with the bulky tri-*o*-tolylphosphine ligand. Such steric effect was observed remarkably at a low temperature of −40°, as described above. It is interesting that an elevation of the temperature increases the relative rates of the paths (a_{11}) and (b_{11}) having the great steric hindrance, as it might be expected.

An increase in the basicity of phosphines seems to accelerate the Markownikoff-type addition of the nickel alkyl to propylene to afford the complex (III) (probably, also for the complex (V)), since an increase of 2,3-DMBs is observed with the increasing basicity. Probably, an increase of the negative charge on the center carbon of *i*-propyl group through the electronic effect of a strong electron-releasing phosphine in the trans site would favor such Markownikoff addition.

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